



Is the thermodynamic behavior of the noble fluids consistent with the principle of corresponding states?

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ABSTRACT

The applicability of the Principle of Corresponding States (PCS) for the noble fluids is discussed. We give the thermodynamic evidence for the dimerization of the liquid phase in heavy noble gases like argon, krypton etc. which manifests itself in deviations from the PCS. The behavior of the diameter of the entropy and the density is analyzed. It is shown that these characteristics are very sensitive to the dimerization process which takes place in the liquid phase of heavy noble gases.

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1. Introduction

The principle of thermodynamic similarity is one of the fundamental guiding principles in investigating the thermodynamic properties of matter. It allows one to determine the classes of substances with similar thermodynamic behavior based on the similarity of the interparticle interactions, which in its turn is based on the similarity of the particles (electronic shells, molecular excitation spectra etc.) and as a consequence the similarity of the interparticle interactions. The existence of the universality classes of critical behavior can be considered as an extension of the thermodynamic similarity principle to the long range fluctuations since the short range effects do not change the asymptotic behavior of the thermodynamic quantities. In particular, for systems obeying the thermodynamic similarity principle the dimensionless critical amplitudes should coincide. The demand of the thermodynamic similarity and as a consequence the principle of corresponding states (PCS) is a very strong condition which in fact assumes the similarity of the energy spectrum of the systems since the thermodynamics depends on both the external and the internal molecular degrees of freedom.

It is well known that the thermodynamics is determined by the integral characteristics of the interaction potential. The classical PCS states the trivial fact that if the interaction potential is of two-particle character and has the form:

$$U_{ij} = U_0 f(r_{ij}/r_0), \quad (1)$$

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Table 1

Basic geometric and energetic parameters of the dimers and the molecules. Notations: r^{vdW} is the van der Waals radius of the molecule, l_{bond} bond length of the dimer, $\varepsilon_{\text{diss}}/T_c$ is the dissociation energy of the dimer in units of T_c , Z_c is the compressibility factor.

	He	H ₂	Ne	Ar	Kr	Xe
r^{vdW} , Å	1.40	1.54	1.54	1.88	2.02	2.16
l_{bond} , Å [1,2]	–	4.2	3.10	3.76	4.01	4.36
$\varepsilon_{\text{diss}}/T_c$, [3,2]	0.0	0.11	0.95	0.96	0.96	0.97
$Z_c = \frac{P_c v_c}{T_c}$	0.30	0.30	0.30	0.29	0.29	0.29
N_{vib} , [4]	–	2	3	8	13	21

where U_0 is the depth of the potential well and r_0 is the characteristic molecular size correspondingly, then the corresponding equation of state (EOS) has the universal dimensionless form

$$p^* = p(v^*, T^*).$$

Here $p^* = Pr_0^3/U_0$ is the dimensionless pressure P , $T^* = T/U_0$ and $v^* = v/r_0^3$ are the dimensionless temperature T and the specific volume v correspondingly. In particular the locus of the critical point (CP) depends on the potential depth U_0 and the molecular radius (hard core radius). Also it is expected that the locus of the triple points for the systems in the coordinates (v^*, T^*) are the same too. The famous van der Waals (vdW) equation of state is an illustration of the PCS. Throughout the paper we use the units where $k_B = 1$.

It is sure that such a simple form of the interparticle interaction is nothing more than an oversimplification since the classical potential $U(r)$ is the effective interaction. It is obtained via integrating out the electronic degrees of freedom and in fact becomes dependent on the atomic number A and the de Boer parameter $\Lambda = \frac{h}{r_0 \sqrt{m U_0}}$ (note that $m = A m_p$, where m_p is the proton mass). For the noble fluids the latter varies in a wide range from $\Lambda_{\text{He}} = 2.7$ to $\Lambda_{\text{Xe}} = 0.06$ [5,6,4].

Nevertheless the quantum effects manifest themselves in a dual way: (a) the corrections to the asymptotic of classical interaction [1]; (b) the formation of bound states (e.g. dimers, trimers etc.). In the first case the potential conserves its essential structure. The bound states lead to additional contributions to the basic thermodynamic quantities (the specific volume, heat capacity etc.). The system becomes the mixture of monomers, dimers etc. The formation of dimers in noble gases is known [3]. It manifests itself in various effects based on the anisotropy structure of the dimers, e.g. in Raman spectra [7–9], depolarization of the light scattering [10,11] etc. But their existence in liquid phase near the CP has not been discussed. Note that the dimers have finite lifetimes but in equilibrium there is certain amount of them.

As follows from the Table 1 the number of the vibrational levels $N_{\text{vib}}(U_0)$ is different for heavy noble gases. The dimerization breaks the PCS. The manifestation of this effect is expected in the gaseous phase of low density (see below). But the degree of dimerization is low for dense liquid states. Only in the vicinity of the critical point could the contribution from the dimers be great enough to break the applicability of the PCS.

Because of the complete electronic shells and as a consequence the spherical symmetry of the ground state, the noble fluids are ideal substances for a test of the PCS.

The aim of this paper is an analysis of the applicability of the PCS for noble fluids and the interpretation of the data from the point of view of dimerization processes in these substances. More exactly we analyze (1) the applicability of the PCS for the description of noble gases on their coexistence curves; (2) the manifestation of the dimerization effects on the temperature behavior of their diameters; (3) the influence of dimerization on the peculiarities of the critical fluctuations.

The aim of this work is to give the evidence of the existence of dimers in near critical region in the liquid phase of the noble fluids. Based on the thermodynamical data for the density, the entropy and the specific heat we estimate the dimerization degree of the noble fluids. In accordance with this, Section 2 is devoted to a careful analysis of the experimental data (all the data are from the NIST open database). The mean field behavior of the diameter for the density and the entropy is considered in Section 3 and the critical anomaly is discussed in Section 4. In Appendix A we discuss the choice of a candidate for the reference system. In Appendix B we consider a simple model to account for the dimerization process for noble fluids.

2. Experimental facts

In this section we discuss: (1) the comparable behavior of the coexistence curves (CC) for noble fluids; (2) the behavior of the number density along the CC. Further we will use the variables reduced to the CP values:

$$\tilde{p} = P/P_c, \quad \tilde{T} = T/T_c, \quad \tilde{n} = n/n_c.$$

First we consider the role of the quantum effects in the EOS. On Fig. 1 we give the CC in “ $\tilde{p} - \tilde{T}$ ” coordinates for classical noble fluids (Ne, Ar, Kr, Xe) and the quantum ones (He and H₂). We see that in “ $\tilde{p} - \tilde{T}$ ” coordinates the classical noble fluids obey the PCS. The deviation from the classical behavior is connected with quantum effects. They are greater for He than for molecular hydrogen. Note that “ $\tilde{p} - \tilde{T}$ ” diagram is the robust thermodynamic characteristics which does not allow one to distinguish fine details of the thermodynamic behavior. The variables \tilde{n} , \tilde{T} are more suitable in this sense.

Let us consider the dimensionless ratio $R(2, 1) = \tilde{n}_2/\tilde{n}_1$ of the dimensionless densities of noble fluid “2” to the density of noble fluid “1”, which is chosen as the reference fluid. The standard choice for such fluid is Ar. The results of a comparison for the liquid and gaseous branches of Kr and Xe with respect to Ar are presented in Fig. 2. As is seen the deviation of the

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